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Extraction of naphthenic acid from highly acidic oil using phenolate based ionic liquids

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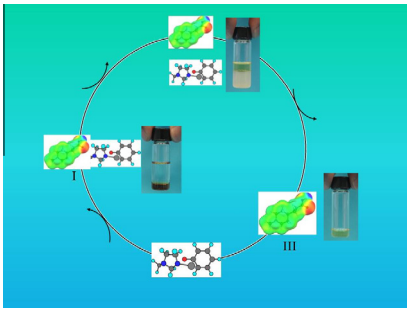
HIGHLIGHTS

- The extraction of naphthenic acid from highly acidic model oil was achieved.
- Very low ionic liquid/model oil ratio is necessary for the complete extraction of naphthenic acid.
- Phenolate based ionic liquids were reused three times without losing its activity significantly.
- COSMO-RS calculations were performed to get more insight into the extraction performance of phenolate based ionic liquids.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, N-alkyl imidazolium ionic liquids with highly alkaline phenolate anions were used for the removal of naphthenic acid from model acid oil. The effect of alkyl spacer length on the deacidification process was evaluated by attaching butyl, hexyl, octyl, decyl and dodecyl groups on imidazolium cation. It was found that increase in the alkyl chain length increases the percent naphthenic acid removal. Extremely low amount of ionic liquids were necessary for the complete deacidification of model oil with high TAN. The reusability of the phenolate ionic liquids was also investigated. COSMO-RS calculations were performed on phenolate ionic liquids to study their extraction efficiency, selectivity and solvent capacity.

1. Introduction

The world heavy crude oil demand is increasing because of the enhanced exploitation and utilization of oil resources in the world. The world's high-acidity crude oil production has increased by 0.3% per year during the recent years [1]. Naphthenic acid present in heavy crude oil is a major source of corrosion in most of the oil refineries around the world. The acidity of the crude oil is expressed in Total Acid Number (TAN), which is a measure of the amount of KOH in milligrams needed to neutralize one gram of crude oil.

Although several methods such as adsorption, solvent extraction, esterification, catalytic decarboxylation, and thermal decom-

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position were available for deacidification of crude oil, soda wash method is considered as the most economical and efficient method for treating the acid streams from refinery [2,3]. The liquid-liquid extraction (LLE) and adsorptive recovery using ion exchange is a widely used laboratory method for recovery of naphthenic acid from crude oil [4,5]. Acidity reduction for highly acidic crude is achieved using thermal and catalytic decarboxylation [6,7]. The catalytic esterification using SnO/Al_2O_3 had been used for crude oil as well as for the diesel streams [8,9]. The lack of process efficiency and loss of higher distillate streams restricts the use of this method. The ion exchange method can be applied only for low temperature lighter distillate fractions and the generation of organic solvent waste restrict the use of liquid–liquid extraction method. The higher temperature that leads to corrosion problems limits the use of decarboxylation process. In order to overcome all these problems, an environmentally friendly and industrially viable technique is required for the processing of high acidity streams.

Recently, Ionic liquids (ILs) has attracted significant attention due to their promising and unique properties such as almost zero volatility, mostly nonflammable, good thermal stability, wide electrochemical window, and wide liquid range. The area of application of ILs includes purification, electrochemistry, extractions, catalysis, etc. [10–14]. The application of ILs have also been reported for naphthenic acid extraction [15–17]. In this study a new class of phenolate anion based ionic liquids with imidazolium cation with varying chain length [$C_n$mim] had been employed for the deacidification of model oil. The phenolate anions were used because of their high basicity and the presence of π electrons, which can enhance the de acidification process. Binnemans et al. used phenolate anion with a *tert*-Butyl group at para position in combination with various cations for the development of a simple method for the synthesis of hydrophilic ionic liquids with very low halide content and highly base stable ammonium ionic liquids [18,19]. Phenolate ionic liquids with tetraalkylphosphonium cation has been used for CO_2 capture [20]. Recently, thermophysical properties of tetramethylguanidinium based ionic liquids with different substituents at para position of the phenol were reported [21]. However, to the best of our knowledge, there were no previous studies conducted on the use of imidazolium based phenolate ionic liquids for the extraction of naphthenic acid from model oil.

2. Experimental

2.1. General information

All the ILs used in this study were synthesized and characterized according to the previously reported literature procedure [22]. All the chemicals were purchased from Acros Organics (Geel, Belgium) or from Sigma–Aldrich (Bornem, Belgium) and were used as received, without further purification.

2.2. Preparation of model acid oil

The simulated acid oil (referred to as model oil) was prepared by adding a certain amount of naphthenic acid to dodecane. The Total acid number of 1.44 (±0.01) was attained and this value is considered as highly acidic based on the normal criteria used for crude oil. Most of the world commercial naphthenic acid is produced from kerosene and diesel fractions of the vacuum column. Dodecane is used as the representation of the kerosene and diesel fractions. The ASTM (American Society for Testing and Materials) D664 method, which is commonly used in the industry to calculate the Total Acid Number (TAN), was employed. Metler Toledo Auto titrator was used to calculate the total acid number according to the ASTM D664 method.

2.3. Deacidification process

The deacidification of model oil was performed by adding 10 g of dodecane and ionic liquid to a round bottom flask which is heated by a hot plate. A magnetic stirrer is used for stirring the mixture and a reflux condenser is attached at the top of the flask. The mixture was stirred at a constant temperature with a stirring rate of 500 rpm for a duration of one hour. The process temperature was optimized by applying different temperature settings. After one hour the reaction mixture was transferred to a separation funnel where it was kept for one hour to achieve a clear separation between the ionic liquid and the model oil. Deacidified oil was collected from the top of the separation funnel to compute the TAN. The percent naphthenic acid removal was calculated using the formula stated below:

$$\text{Percent Naphthenic Acid Removal} = (1 - \text{Tan}_f \div \text{Tan}_i) \times 100$$

where TAN_f and TAN_i refer to final and initial TAN of the oil respectively.

2.4. Computational details

The computational details of the COSMO-RS are given as follows. For structural optimization of the cations and phenolate anion, TmoleX 3.1 (Turbomole Version 6.2) [23] quantum mechanics package was used. The structure of the phenolate anion, cations and naphthenic acids were drawn using COSMO build 1.5. The geometry optimization for naphthenic acids were performed at the density functional theory (DFT) level, utilizing the BP functional [24–26] with resolution of identity (RI) approximation and a triple-ξ valence polarized basis set (TZVP) [27,28]. For the prediction involving ionic liquids, electro neutral mixture approach was assumed. That is, cations and anions are treated separately in COSMO calculations by assuming equimolar composition of cations and anions. The geometry optimizations of the ionic liquids were performed using dispersion corrected DFT (DFT-dsp) methods as the interaction in ionic liquids are influenced significantly by dispersion forces [29]. COSMO-RS calculations were performed using the COSMOthermX programme (Version C21) with BP_TZVP_C21_0111.ctd parameterization. Activity coefficients at infinite dilutions of naphthenic acids and dodecane (model oil) were calculated at 298.15 k. The details about the COSMO-RS model along with the expression for activity coefficient in the liquid phase are described elsewhere [30]. The COSMO-RS theories for predictions have been extensively explained in the literature [31,32]. Selectivity and solvent capacity were calculated from the activity coefficient values.

3. Results and discussion

3.1. Effect of reagent/oil ratio

An overview of ILs used in this study is given in Fig. 1. Ionic liquids/oil ratio is one of the deciding factors in the de-acidification process. The effect of ionic liquid/model oil ratio on deacidification process was investigated. The percent naphthenic acid removal was calculated with different weight ratios. The extraction time was one hour, followed by a 1 h separation time. The effect of different reagent to oil ratio is given in Table 1 and Fig. 2.

As the ionic liquid/model oil ratio increases, there is a clear increase in the percent of naphthenic acid extraction for all types of ionic liquids. It was found that at room temperature, [C_{10}mim]

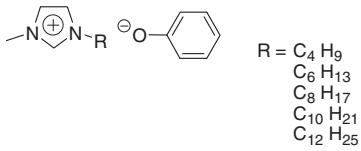

Fig. 1. Overview of ionic liquids used in this study.

[Phe] was the most effective in naphthenic acid extraction among the ionic liquids under investigation. When the ionic liquid/model oil ratio was increased from 0.01 to 0.02, the extraction performance of [C_{12}mim][Phe] and [C_{10}mim][Phe] increases up to about 80% from less than 40%. While, extraction performance of the other ionic liquids only increases moderately at the same ionic liquid/-model oil ratio. This observation agreed well with the prediction that the [C_{12}mim][Phe] will show higher extraction efficiency due to the long alkyl spacer length in the cation. Earlier, it has been reported that the naphthenic acid extraction efficiency of ionic liquids increases with an increase in the alkyl spacer on the cation due to the increased *van der Waals* interaction between the alkyl group and naphthenic acid moiety [15]. The ionic liquids [C_4mim][Phe], [C_6mim][Phe] and [C_8mim][Phe] showed 100% efficiency at an ionic liquid/model oil ratio of 0.09. The extraction efficiency of the ionic liquids follows the order [C_{10}mim][Phe] ≈ [C_{12}mim][Phe] > [C_8mim][Phe] > [C_6mim][Phe] > [C_4mim][Phe]. The longer the alkyl groups in the ionic liquids, the greater the extraction efficiency. However, [C_{12}mim][Phe] and [C_{10}mim][Phe] have comparable efficiency. For instance, the extraction efficiency of [C_{12}mim][Phe] and [C_{10}mim][Phe] at an IL/model oil ratio of 0.02 is 77% and 80% respectively. It is more likely due to the higher viscosity of [C_{12}mim][Phe], which hinders the effective mass transport of naphthenic acid thus leading to lower extraction efficiency. The imidazolate anion based ionic liquids with $[C_8mim]^+$ cation showed 100% extraction efficiency at an ionic liquid/model oil ratio of 0.008, while [C_8mim][Phe] requires higher ionic liquid/model ratio (0.09) for complete deacidification of the model oil. However, a highly acidic model oil was employed in this study. The phenolate based ionic liquids have higher extraction performance than N-alkyl pyridinium bromides and 1-alky-3-methylimidazolium bromides [15,17]. For instance, 1-octyl-3-methylimidazolium bromide, [C_8mim][Br], extracted only 93% of naphthenic acid from a model oil with an ionic liquid/model oil ratio of 0.1, even if the acidity of the model system was very low(<0.5 TAN). At the similar conditions, 1-octylpyridinium bromide extracted less than 65% of naphthenic acid. The comparison of extraction efficiency of various ionic liquids is given in Table 2.

3.2. Effect of temperature on naphthenic acid extraction

After optimizing the IL/oil ratio for the extraction process, the effect of temperature on the deacidification was investigated using

Table 1
Effect of IL/oil ratio on percent naphthenic acid removal.

IL/oil ratio	Percent naphthenic acid removal				
	[C_4 mim] [Phe]	[C_6 mim] [Phe]	[C_8 mim] [Phe]	[C_{10} mim] [Phe]	[C_{12} mim] [Phe]
0.01	15	17	20	39.48	33.22
0.02	41.3	44.6	46.25	80	77
0.03	50.45	54.91	55.275	100	100
0.04	60	65.21	65.86	100	100
0.05	69.48	71.98	72.44	100	100
0.06	78.54	78.75	79.13	100	100
0.07	87.75	87.97	88.25	100	100
0.08	96.38	96.45	96.97	100	100
0.09	100	100	100	100	100

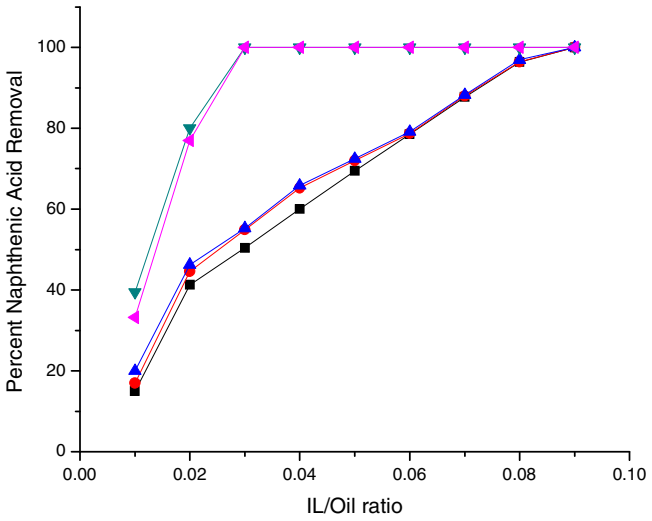

Fig. 2. Effect of IL/model oil ratio on extraction efficiency of naphthenic acid removal (■, [C_4mim][Phe]; ●, [C_6mim][Phe]; ▲, [C_8mim][Phe]; ▼, [C_{10}mim][Phe]; ◄, [C_{12}mim][Phe]) (stirring rate, 500 rpm; reaction time, 1 h).

[C_{10}mim][Phe] and [C_{12}mim][Phe] within the temperature range of 303.15–383.15 K due to their superior performance over other ionic liquids. All other extraction conditions were kept unchanged. As displayed in Fig. 3, the percent naphthenic acid removal showed an increasing trend with the increase in temperature at a fixed IL/oil ratio (0.02 wt%).

The experimental results shows that viscosity is serving as a barrier to the efficiency of the process by lowering the mass transport of the solute. Once the viscosity is reduced by increasing the temperature, an efficient mixing was occurred and the extraction

Table 2
Naphthenic acid extraction efficiency of different ionic liquids.

Ionic liquid	IL/oil ratio	Extraction efficiency (%)	References
1-Ethylpyridinium bromide [EPy][Br]	0.1	3.47	[15]
1-Butylpyridinium bromide [BPy][Br]	0.1	27.76	[15]
1-Hexylpyridinium Bromide [HPy][Br]	0.1	55.17	[15]
1-Octylpyridinium bromide [OPy][Br]	0.1	64.44	[15]
1-Ethyl-3-methylimidazolium bromide [Emim][Br]	0.1	26.76	[15]
1-Butyl-3-methylimidazolium bromide [Bmim][Br]	0.1	34.54	[15]
1-Hexyl-3-methylimidazolium bromide [Hmim][Br]	0.1	63.24	[15]
1-Octyl-3-methylimidazolium bromide [Omim][Br]	0.1	93.22	[15]
1-Ethyl-3-methylimidazolium imidazolate [Emim][Im]	0.016	100.0	[17]
1-Butyl-3-methylimidazolium imidazolate [Bmim][Im]	0.012	100.0	[17]
1-Hexyl-3-methylimidazolium imidazolate [Hmim][Im]	0.010	100.0	[17]
1-Octyl-3-methylimidazolium imidazolate [Omim][Im]	0.008	100.0	[17]
1-Butyl-3-methylimidazolium phenolate [C_4mim][Phe]	0.03	50.45	This work
1-Hexyl-3-methylimidazolium phenolate [C_6mim][Phe]	0.03	54.91	This work
1-Octyl-3-methylimidazolium phenolate [C_8mim][Phe]	0.03	55.275	This work
1-Decyl-3-methylimidazolium phenolate [C_{10}mim][Phe]	0.03	100.0	This work
1-Dodecyl-3-methylimidazolium phenolate [C_{12}mim][Phe]	0.03	100.0	This work

efficiency enhanced remarakably. The optimal process temperature for deacidification using [C_{10}mim][Phe] was found to be 323 K, while the maximum efficiency was achieved at 343 K for [C_{12}mim][Phe], which is higher than the efficiency of [C_{10}mim][Phe] at similar conditions. The increase in the extraction efficiency of [C_{12}mim][Phe] with temperature is not as significant as in [C_{10}mim][Phe]. When the temperature increases from 303.15 K (viscosity is 200.94 cP) to 323.15 K (viscosity is 77.54 cP), the extraction performance of [C_{10}mim][Phe] was increased by more than 5%. However, only 1% increase in extraction performance was observed for [C_{12}mim][Phe]. Nevertheless, a significant increase in the extraction performance (>6%) was observed for [C_{12}mim][Phe] when the temperature was raised to 343.15 K. The increase in the extraction efficiency of [C_{12}mim][Phe] can be explained by the decrease in viscosity as temperature increases thus ensuring a more efficient mixing that enhances mass transfer between the two phases. However, there is a temperature limit beyond which the extraction efficiency of both ionic liquids will begin to decrease. In order to ensure that the ionic liquids did not decompose at the highest temperature applied in the study, a ^{1}H NMR spectroscopy was conducted on the ionic liquids sample after extraction. From the spectra obtained (Figs. 1 and 2 in supporting information), it can be said that the two ILs still remain intact even at high temperature i.e., 383.15 K.

3.3. Repetitive reaction of ionic liquids

The reusability of the ionic liquids for extracting the naphthenic acid is an important criteria in determining their potential for industrial applications. The extent of reusability of the ionic liquids could have a reflection on the sustainability of the process. In the current study, the reusability of ionic liquids was investigated using [C_{10}mim][Phe] and [C_{12}mim][Phe] with the optimized IL/oil ratio of 0.04 at room temperature. The model system having a TAN strength of 0.6 mg KOH/gm of oil was used. After each cycle of extraction, the model oil was completely removed and the percentage of naphthenic acid removal was calculated from the TAN measurement. Fresh model oil was then added to the used ionic liquids and the procedure was repeated until the percent naphthenic acid removal drops to below 30%. The results from the experiment is shown in Fig. 4. In general, the two phenolate ionic liquids could be recycled up to three times without significant decline in their extraction efficiency i.e., efficiency remains above 80%. Even after seven cycle of extraction, the phenolate ionic liquids were still showing efficiency of more than 35%. As for the comparison between the two ionic liquids, the [C_{10}mim][Phe] and [C_{12}mim][Phe] demonstrated comparable performance in the reusability study which was similar to the findings earlier for the single cycle extraction although it is evident that in the third cycle, the efficiency of the [C_{10}mim][Phe] is slightly higher compared to [C_{12}mim][Phe].

3.4. Effect of different total acid number of oil

The effect of different TAN strengths of the model oil on the extraction efficiency of ionic liquids were studied using [C_{10}mim][Phe] using the optimized IL/oil ratio of 0.04 and the results are shown in Fig. 5. The TAN strength of the model oil was increased by adding more naphthenic acid to the model oil.

The reaction and separation time was kept at one hour for the experiments. The [C_{10}mim][Phe] was found to completely deacidify the model oil up to a TAN value of 2.0 mg KOH/g. However, as the TAN value of the model oil was increased from 2 mg KOH/g to 5 mg KOH/g, there was slight reduction in the extraction efficiency. Although the TAN value of the model oil was increased up to 5 mg KOH/g in the experiment, the deacidification achieved was still above 25% which indicates the potential application of the phenolate based ionic liquids to deacidify highly acidic crude oil.

3.5. Mechanism of naphthenic acid extraction

The phenolate ionic liquids were successful in the removal of the naphthenic acid primarily because of their basicity due to the presence of phenolate anion. The pKa value of phenolate anion is 10 and the degree of basicity for compounds increases with larger pKa value [20]. In addition, it has been reported that ionic liquids could also behave as liquid clathrate sustaining media [33], i.e., the solute molecules can be trapped into the cage structure formed by the ionic liquids as a results of the π–π interaction between the solute molecules and ionic liquids system. Since there are six π electrons presence in the phenolate anion, the interaction with

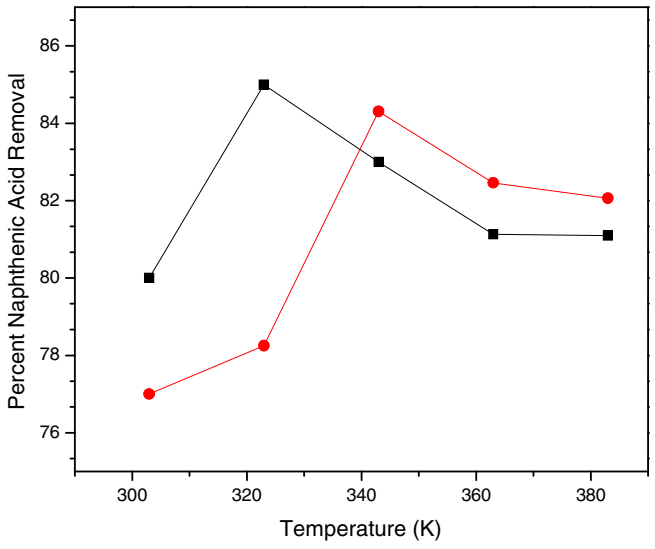

Fig. 3. Effect of temperature on naphthenic acid extraction (■, [C_{10}mim][Phe] with 0.02 IL/oil ratio; ●, [C_{12}mim][Phe] with 0.02 IL/oil ratio) (stirring rate, 500 rpm; reaction time, 1 h).

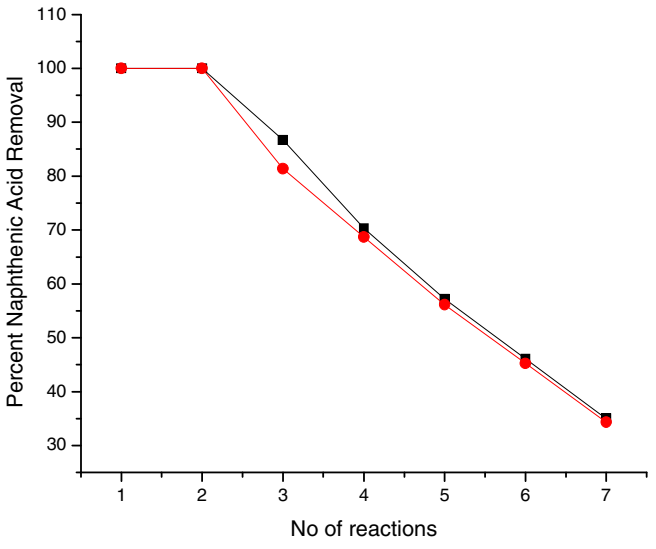

Fig. 4. Reusability of ionic liquids (■, [C_{10}mim][Phe] with 0.04 IL/oil ratio; ●, [C_{12}mim][Phe] with 0.04 IL/Oil ratio) (temperature, 303 K; stirring rate, 500 rpm; reaction time, 1 h).

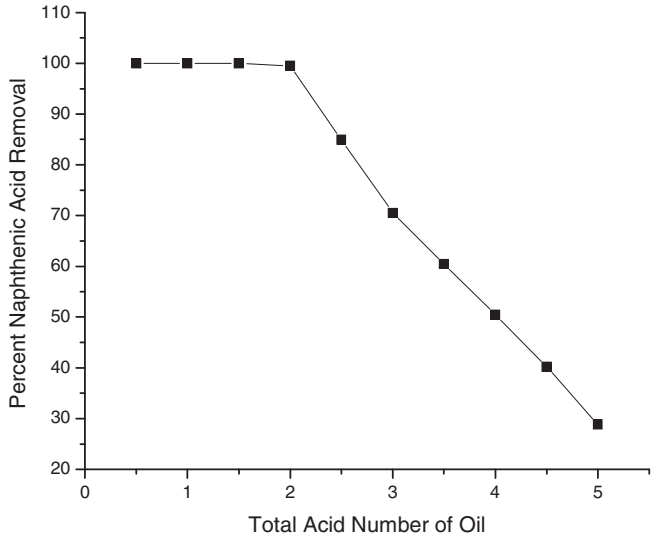

Fig. 5. Effect of increase in total acid number on extraction efficiency of naphthenic acid (■, [C_{10}mim][Phe] with 0.04 IL/oil ratio) (temperature, 303 K; stirring rate, 500 rpm; reaction time, 1 h).

the unsaturated bonds within the naphthenic acids structure is expected to be higher. This will further enhance the capture of the naphthenic acid molecules into the cages, leading to increased naphthenic acid extraction. Also, as the alkyl spacer length in the imidazolium cation increases, more space will be created in the cage, which in turn leads to the increasing ability to trap more naphthenic acid. This also augurs well with the fact that increasing the alkyl spacer length of the cation will also increase the basicity of the ionic liquids [15], hence enabling better extraction of the naphthenic acid. The extent of reusability of the ionic liquids can also be related to the size of the cage formed in the ionic liquids. From the reusability experiments, it was speculated that multiple naphthenic acid molecules can be trapped into the cages formed in ionic liquids. Hence the ionic liquids can be reused several times even without any recovery. However, high temperature is not favourable for the naphthenic acid extraction (Fig. 3) and this could be likely due to the higher energy possessed by the naphthenic acid molecule and therefore increasing its probability to escape from the cage structure. Thus, the extraction performance was found to decrease beyond a particular temperature.

3.6. Quantum chemical calculations

COSMO-RS model was used to understand the effect of structural variations of the ionic liquids and nature of the naphthenic acids on the extraction process. The structure of the naphthenic acids used in this study are shown in Fig. 4 in supporting information. The activity coefficients at infinite dilution of the solutes i.e., naphthenic acids and dodecane (model oil), in the ionic liquids were calculated at 298.15 K and are shown in Fig. 6.

All the naphthenic acids used in the study showed a much lower activity coefficient compared to the dodecane (model oil). Lower activity coefficient reflects stronger interaction between the ionic liquids and the naphthenic acids than with dodocane, which explains the extraction preference of the naphthenic acids by the ionic liquids. The activity coefficient of the solutes in the ionic liquids depends on the alkyl spacer length of the imidazolium cation. The order of the activity coefficient of the naphthenic acids and dodecane follows the order of [C_{12}mim][Phe] < [C_{10}mim][Phe] < [C_8mim][Phe] < [C_6mim][Phe] < [C_4mim][Phe]. The lowest activity coefficient value was observed for [C_{12}mim][Phe] which means that [C_{12}mim][Phe] is expected to have the strongest interaction with the naphthenic acids compared to the others. This is in agreement with the experimental results where [C_{12}mim][Phe] showed the highest efficiency especially at higher temperature for the extraction of naphthenic acid from model oil.

The activity coefficient of naphthenic acids in the ionic liquids also depends on the nature of the acids. Increasing the number of carbon atoms in naphthenic acids from C_{10} ($C_{10}H_{20}O_2$) to C_{15} ($C_{15}H_{30}O_2$) increases the activity coefficient values, which implies that longer alkyl chain naphthenic acids are less soluble in the ionic liquids used. For naphthenic acids with the same number of carbon atoms, changing from straight chain to cyclic structure does not significantly affect their activity coefficients. This can be observed from the activity coefficients values of $C_{10}H_{20}O_2 \approx C_{10}H_{18}O_2$–$C_5 \approx C_{10}H_{18}O_2$–$C_6$ and $C_{15}H_{30}O_2 \approx C_{15}H_{26}O_2$–$C_5 \approx C_{15}H_{26}O_2$–$C_6$. This shows the interaction of the naphthenic acids with ionic liquids depends mainly on the alkyl chain length of the acids irrespective of its cyclic or acyclic nature. Naphthenic acids with lower number of carbon atoms interact strongly with ionic liquids and hence their solubility will be higher.

Activity coefficient accounts only to the extent of interaction between the ionic liquids and the solutes and does not reflect their extraction ability. Solvent with good naphthenic acid extraction capability should strongly interact with naphthenic acids (low

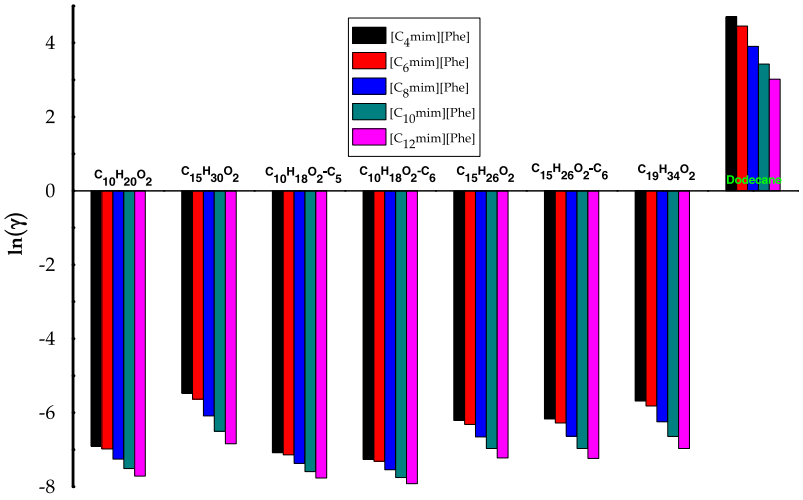

Fig. 6. Activity coefficients of the naphthenic acids and dodecane in the studied ionic liquids.

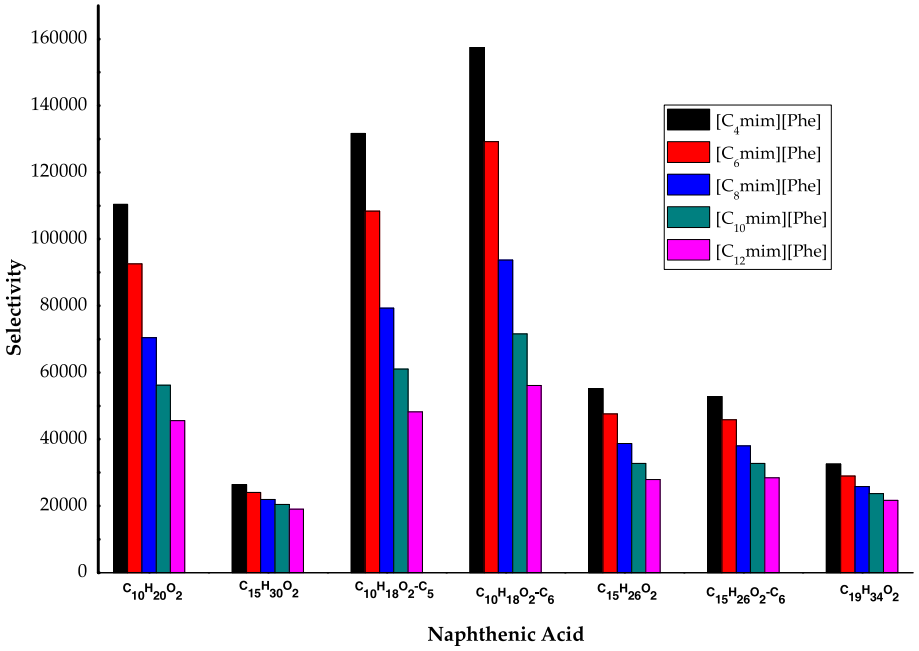

Fig. 7. Selectivity of ionic liquids for naphthenic acid as compared to dodecane.

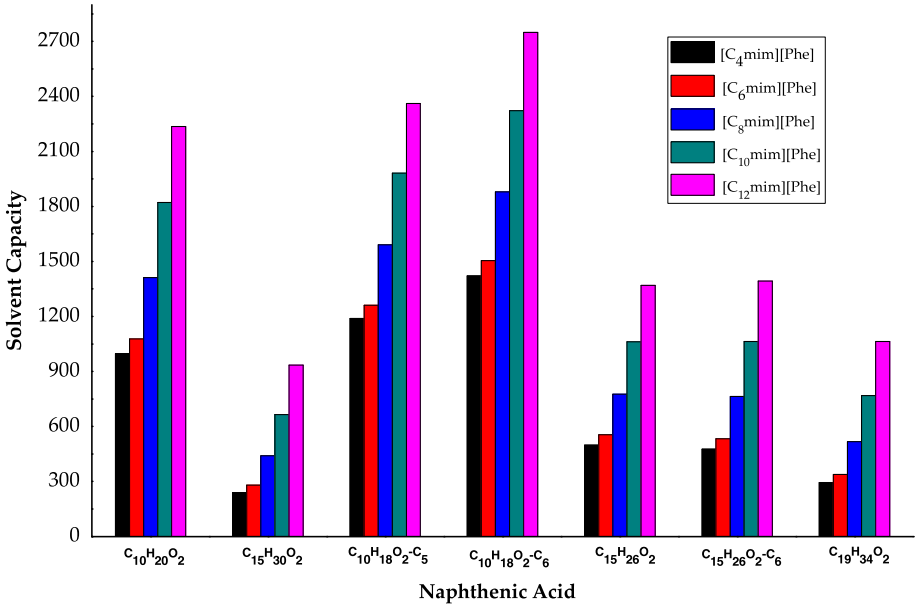

Fig. 8. Capacity of ionic liquids for naphthenic acid.

naphthenic acid activity coefficient), and should have less interaction with dodecane (high dodecane activity coefficient). This can be expressed in terms of selectivity of ionic liquids for naphthenic acids compared to dodecane. Selectivity at infinite dilution can be expressed in terms of activity coefficient as shown in the following equation.

$$S_{nd}^{\infty} = \frac{\gamma_d^{\infty}}{\gamma_n^{\infty}}$$

where, S_{nd}^{∞} is selectivity of ionic liquids for naphthenic acids compared to dodecane, γ_d^{∞} and γ_n^{∞} are the acvity coefficients of dodecane and naphthenic acids, respectively. The S_{nd}^{∞} values are plotted in Fig. 7.

Selectivity decreases with an increase in alkyl spacer length in imidazolium cation. As the alkyl spacer length increases, the *van der Waals* interaction between the ionic liquids and dodecane increases. This can be observed from the activity coefficients of dodecane and naphthenic acids, which is higher for longer alkyl chain ionic liquids. The selectivity of ionic liquids for naphthenic acids follows the order [C_{12}mim][Phe] < [C_{10}mim][Phe] < [C_8mim][Phe] < [C_6mim][Phe] < [C_4mim][Phe] irrespective of the type of naphthenic acids used. However, the change in selectivity with imidazolium alkyl chain depends on the nature of the naphthenic acids. The selectivity decreases as the number of carbons in the naphthenic acid increases. Moreover, ionic liquids are more selective toward cyclic naphthenic acid than non-cyclic analogues. This can be observed from selectivity values of $C_{10}H_{20}O_2 < C_{10}H_{18}O_2{-}C_5 < C_{10}H_{18}O_2{-}C_6$ and $C_{15}H_{30}O_2 < C_{15}H_{26}O_2{-}C_5 < C_{15}H_{26}O_2{-}C_6$.

3.7. Solvent capacity

Although selectivity is an important parameter for the selection of solvents for extraction, it does not convey any information regarding the amount of solvent required for the extraction. The amount of solvent required for the extraction can be qualitatively expressed in terms of solvent capacity and the solvent capacity at infinite dilution can be calculated from activity coefficient of the target solute using the following equation.

$$C_n^{\infty} = \frac{1}{\gamma_n^{\infty}}$$

where, C_n^{∞} is solvent capacity of ionic liquids for naphthenic acids and γ_n^{∞} are the activity coefficients of naphthenic acids. The plot of C_n^{∞} versus naphthenic acids for the studied ionic liquids are shown in Fig. 8.

The solvent capacity increases with increasing alkyl chain length of ionic liquids cation. The order of solvent capacity for ionic liquids based on C_n^{∞} is [C_{12}mim][Phe] > [C_{10}mim][Phe] > [C_8mim][Phe] > [C_6mim][Phe] > [C_4mim][Phe]. The highest capacity was observed for the phenolate ionic liquids with an alkyl spacer length of twelve carbon atoms and ionic liquids with a butyl group showed the lowest selectivity. On the contrary, the increase in the number of carbon atoms in naphthenic acid decreased the capacity. For instance, in straight chain naphthenic acid, the solvent capacity of [C_{12}mim][Ph] was reduced from 2200 to 900 when the alkyl chain length increased from C_{10} to C_{15}. Another interesting observation is that the solvent capacity of ionic liquids for cyclic naphthenic acids is higher than their corresponding noncyclic analogue. This is directly related to the *van der Waals* interaction and ring similarity as mentioned before.

4. Conclusion

The phenolate based ionic liquids are very effective in the deacidification of high TAN model oil with a extremely low ionic liquid/oil ratio. Imidazolium cation with alkyl groups such as butyl, hexyl, octyl, decyl and dodecyl were used to study the effect of alkyl groups on extraction efficiency. The extraction efficiency of the phenolate ionic liquids increases with an increase in the alkyl spacer length on the imidazolium cation. [C_{10}mim][Phe] showed maximum extraction efficiency. All the ionic liquids can be reused more than three times for the extraction without compromising their extraction performance. Quantum mechanical calculations were used to get more insight into the interaction of ionic liquids with napthenic acids and the theoretical studies revealed that [C_{12}mim][Phe] has the maximum extraction efficiency, selecticity and solvent capacity for the napthenic acid extraction.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2015.09.017.

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